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## Highly efficient 2D siloxene coated Ni foam catalyst for methane dry reforming and an effective approach to recycle spent catalyst towards energy storage application

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### **ABSTRACT:**

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The dry reforming of methane (DRM) using CO<sub>2</sub> for the production of syngas (H<sub>2</sub> and CO) received increasing attention for reducing the global CO<sub>2</sub> emission and capability of the chemical energy transmission system. The main drawback of DRM reactions is the limited reusability of the spent catalyst due to carbon deposition on their surface. Thus, designing an appropriate catalytic system are adequate to achieve increased syngas production with low carbon deposition and developing smart strategies to reuse the carbon deposited spent catalyst is highly desirable. In this work, two dimensional siloxene sheets (silicon analog of graphene oxide) coated nickel foam is examined as a novel catalyst for DRM reaction. The siloxene/Ni foam catalyst demonstrated superior catalytic performance in terms of conversion efficiencies (for CH<sub>4</sub> and CO<sub>2</sub>) and syngas production (H<sub>2</sub> and CO) with a high H<sub>2</sub>/CO ratio of 1.5. Further, the carbon deposited siloxene/Ni spent catalyst recovered after DRM reaction was effectively reutilized as electrodes for symmetric supercapacitor (SSC) using organic electrolyte. The fabricated SSC (using spent catalyst as electrodes) delivered a high device capacitance (24.65 F g<sup>-1</sup>), high energy density (30.81 Wh Kg<sup>-1</sup>), and high-power density (15,625 W kg<sup>-1</sup>) with long cycle life. Considering the estimated carbon cost for developing a supercapacitor electrode is about \$15 per kilogram, our strategy to effectively reutilize the recovered carbon deposited spent catalyst for energy storage applications might be a promising and economical approach for utilization of spent catalyst.

**KEYWORDS:** Siloxene sheets; Dry reforming of methane; Spent catalyst; Supercapacitor; Energy density.

### 1. Introduction:

The depletion of fossil fuels and increased concentration of greenhouse gases from the beginning of the industrial revolution resulted in global warming and anthropogenic climate change <sup>1-3</sup>. The increasing atmospheric concentration of greenhouse gases (GHG) such as carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O) and fluorinated gases is one of the major cause for the extreme weather events, global climatic changes, and environmental effects (increased sea water-level and the increasing number of ocean storms, floods)<sup>4</sup>. The conversion of GHGs into useful energy/products is of prime interest in order to solve the global warming issue <sup>5,6</sup>. Herein, the dry reforming of methane (DRM) reaction is promising since it can convert two GHGs (CH<sub>4</sub> and CO<sub>2</sub>) into energy-rich mixtures<sup>7,8</sup>. The DRM reaction results in the formation of the synthetic gas or syngas (H<sub>2</sub> and CO) which can be utilized for energy production and preparation of valuable chemicals via Fischer-Tropsch synthesis <sup>9,10</sup>. The DRM reaction usually occurs in the presence of metal- based catalysts at high temperatures (700 to 1000 °C) due to the chemical inertness and thermodynamic stability of CH<sub>4</sub> and CO<sub>2</sub> molecules <sup>11</sup>. Among the various metal catalysts, metallic nickel (Ni) showed superior catalytic performances for DRM reaction with the advantage of being low cost over other noble metals <sup>12</sup>. Hitherto, the side reactions involved the DRM process such as (i) reverse water gas shift reaction (RWGS)<sup>13</sup>, (ii) carbon gasification <sup>14</sup>, (iii) CH<sub>4</sub> decomposition reaction <sup>11</sup>, and (iv) Boudouard reaction <sup>15</sup>, which severely affects the catalyst performance and deactivation which is mainly due to carbon deposition after DRM reaction <sup>16</sup>. In order to prevent these side reactions, several surface modification of metallic Ni catalyst such as developing bimetallic or hybrid catalyst, using co-catalyst, entrapping Ni in a porous matrix, and confining nano Ni catalyst in meso- or microporous silica have been employed<sup>10,17-20</sup>. Among these, the use of silica as cocatalyst/promoters are widely recognized in the DRM reactions owing to their low-cost, highly abundancy, low-toxicity, and ability to tune shape/morphology <sup>11,21</sup>. However, the development of novel catalyst design with high performance activity with low carbon deposition is highly essential for DRM reactions which is an area of huge interest <sup>22</sup>.

The emergence of two dimensional(2D) materials beyond graphene sheets result in an exceptional performance in energy conversion-, storage- and catalysis sectors <sup>23</sup>. The 2D materials such as graphene oxide, MoS<sub>2</sub>, WS<sub>2</sub>, and boron nitride sheets are widely used as cocatalysts for DRM reaction in the last decade <sup>24-26</sup>. Recently, siloxene sheets (2D-silicon analog of graphene oxide), a direct bandgap material with rich chemistry, and structural integrity become an exciting material for energy storage, environmental remediation, and catalytic applications <sup>27–29</sup>. Considering the catalytic applications of siloxene, at first, Badley et al. explored their use towards ethylene polymerization during 1993<sup>30</sup>. After a long time span, Zhang et al. demonstrated the use of palladium loaded siloxene as a sustainable catalyst for Mizoroki–Heck reaction during 2014<sup>31</sup>. Recent studies highlighted the use of siloxene as a catalyst towards metal-free semiconductor for water splitting, photocatalytic removal, and degradation of nitrogen monoxide, respectively <sup>32,33</sup>. These results demonstrated that the effectiveness of siloxene sheets for various heterogeneous catalytic applications. Based on the intriguing properties of siloxene sheets such as large interlayer spacing, surface functionalized with oxygenated groups, high specific surface area, and plentiful active sites, in this work, we have aimed to explore their applications as co-catalyst for DRM process via coating siloxene sheets on Ni foam.

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Interestingly, the siloxene/Ni foam significantly enhances the catalytic activity of bare Ni foam in terms of methane and CO<sub>2</sub> conversion efficiencies as well as syngas production ranges

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with good stability. The analysis on the spent catalyst shows the carbon deposition after the DRM process due to methane cracking, which limits further reusability of the catalyst. It should be considered that the carbon waste disposal from the spent catalyst is a global concern which can create severe economic and environmental issues in accordance to the resource conversion and recovery act (RCRA)<sup>34</sup>. Hitherto, the carbon deposited spent catalysts are usually disposed via landfill or regeneration strategies such as fouling, poisoning, thermal degradation, and sintering, to make them reusable <sup>20,35</sup>. Moreover, the cost for regeneration of carbon deposited spent catalysts is not economic; thus, more effective routes for re-utilization of spent catalysts are required<sup>20,36</sup>. In order to solve this conundrum, we have also developed a smart strategy to recycle the spent catalyst via examining their use as supercapacitor electrodes. It is notable that the estimated carbon cost for developing a supercapacitor electrode is about \$15 per kilogram<sup>37</sup>. Thus, the regeneration of carbon deposited spent catalysts towards application as supercapacitor electrodes are a more promising strategy. The performance of the carbon deposited spent catalyst electrodes were accessed via fabrication of CR2032 (coin cell) type symmetric supercapacitor (SSC) using 1 M TEABF<sub>4</sub> electrolyte. The fabricated SSC using spent catalyst electrodes demonstrated excellent charge-storage characteristics (comparable to that of reported carbonbased supercapacitors) which makes this approach as a meaningful and economical way to recycle waste to energy (WtE) concepts.

### 2. Results and discussion

The schematic representation (shown in Figure 1(A)) demonstrates the preparation of siloxene sheets via topochemical reaction (similar to the method reported elsewhere)  $^{28}$ . The topochemical synthesis involves two simultaneous reaction pathways viz. (i) removal of Ca atoms and (ii) oxidation of silicon layers present in the CaSi<sub>2</sub> which results in the formation of

2D siloxene sheets <sup>38</sup>. The high-resolution transmission electron micrograph (HR-TEM) of siloxene nanostructures is provided in Figure 1 (B) which revealed the presence of sheet-like morphology (lateral dimension in the range of  $1 \times 1 \ \mu m^2$ ) with a good level of transparency. The elemental mapping analysis of siloxene sheets indicated the homogenous uniform distribution of silicon (Figure 1(C)) and oxygen atoms (Figure 1(D)) throughout the siloxene sheets. The elemental mapping spectrum of siloxene sheets given in Figure 1(E) evidence the presence of Si and O elements (from siloxene sheets) with small fraction of carbon (which arises from carbon grids used for sample preparation). The O/Si atomic ratio of the siloxene sheets is found to be 1.4from the EDS analysis (quantified using Cliff Lorimer thin ratio section method) which is in good agreement with the previous report <sup>39</sup>. The field emission scanning electron microscopic (FE-SEM) images of the prepared siloxene sheets is provided in Figure S1 (A-B), SI suggesting the presences of sheet-like structures and the elemental mapping analysis (Figure S1(C-F), in SI) indicates the presence of Si and O atoms in the siloxene sheets. The FT-IR spectrum of siloxene sheets (Figure S2(A), SI) shows the presence of characteristic bands at 450-515, 880, 1047, 1632, and 215 cm<sup>-1</sup> corresponding to the vibrations of  $v_{(Si-Si)}$ ,  $v_{(Si-O-Si)}$ ,  $v_{(Si-OH)}$ , and  $v_{(O-Si2=Si-H)}$ bonds in the siloxene sheets <sup>32</sup>. This finding indicated the formation of Kautsky-type siloxene sheets (Si<sub>6</sub> rings are interconnected via Si–O–Si bridges in the silicon planes) via the topochemical reaction. The laser Raman spectrum of the siloxene sheets (Figure S2(B), SI) displays the vibrational bands of Si-Si (379 cm<sup>-1</sup>), Si-O-Si (497 cm<sup>-1</sup>), Si-Si (521 cm<sup>-1</sup>), and Si-H (641 and 731 cm<sup>-1</sup>), respectively <sup>28</sup>. In comparison with the Raman spectrum of CaSi<sub>2</sub> (usually, show a sharp Raman band at 515 cm<sup>-1 28</sup>), the Raman spectrum of siloxene sheets shows significant changes which confirm the formation of siloxene sheets. The XPS core-level spectrum of Si 2p and O 1s states of siloxene sheets are provided in Figure S3, SI. The Si 2p

state of siloxene indicates the existence of two peaks at 99.12 and 102.60 eV which arises from the Si-Si and oxygenated Si counterparts of the siloxene sheets. The O 1s spectrum shows the presence of a peak at a binding energy of 532 eV which emerged from the oxygen- and hydroxyl- groups attached to the basal planes and edges of siloxene sheets. The morphological, composition and spectroscopic analysis clearly demonstrated that the topochemical de-intercalation of Ca (from CaSi<sub>2</sub>) results in the formation of siloxene sheets <sup>28</sup>.

Figure 2 depicts the utilization of siloxene sheets coated on Ni foam as a catalyst for DRM reaction for the production of syngas and strategy for effective utilization of spent catalyst as electrodes for SSC. The siloxene/Ni catalyst pellets were packed in the thermocatalytic reactor (Figure S4, SI) used for DRM process and the conversion efficiency and syngas production was monitored via gas chromatography (Figure S5, SI). Figure 3 presents the catalytic properties siloxene/Ni foam in terms of methane and CO<sub>2</sub> conversion into syngas production over the temperature range of 750–900 °C. The conversion efficiency of input gases (methane and  $CO_2$ ) using the siloxene/Ni catalyst as a function of temperature as shown in Figure 3(A) which revealed that the high temperature results in higher conversion efficiency. A maximum conversion efficiency of methane and CO<sub>2</sub> using siloxene/Ni catalyst was found as 85 and 86 % at a temperature of (900 °C). Figure 3(B) depicts the concentration of output syngas (H<sub>2</sub> and CO) catalytically converted by siloxene/Ni catalysts as a function of 750 to 900 °C. At a temperature of 900 °C, the concentration of H<sub>2</sub> and CO was determined as 14.32 and 9.41 v % using the siloxene/Ni foam which is almost 1.36 and 1.56-fold higher than that of the bare Ni foam (Figure S6, SI). The siloxene/Ni catalyst demonstrated superior catalytic property (in terms of both conversion efficiency and syngas production) over bare Ni catalyst and reported silica-based catalysts <sup>40,41</sup>. Table S1 compares the conversion (%) and selectivity of gases using bare Ni foam

and siloxene/Ni foam catalysts. It revealed that the siloxene/Ni catalyst showed high conversion efficiency and enhanced selectivity values, thus, demonstrating the siloxene coating favoring the DRM reactions. This superior catalytic performance of siloxene/Ni foam can be attributed to the high surface area of siloxene sheets which might act as a strong adsorbent of gases, thereby increasing the active sites at the Ni surface. The effect on temperature on the  $H_2/CO$  ratio of the produced syngas concentrations using siloxene/Ni catalyst is summarized in Figure 3(C). The H<sub>2</sub>/CO ratio was increased from 1.05 % and reached a maximum of 1.5 % when the temperature is increased from 750 to 900 °C, respectively. The higher  $H_2/CO$  ratio of 1.5 % (which is above unity) might be ascribed due to the side reactions (methane cracking or water gas shift reaction) occurred during the DRM process <sup>42</sup>. However, these values are suitable for the production of liquid hydrocarbons via the Fischer-Tropsch synthesis and the production of oxygenated hydrocarbon compounds  $^{43,44}$ . Thus, from a practical point of view, the obtained H<sub>2</sub>/CO ratio via the DRM process using siloxene/Ni is industrially worthwhile for various applications <sup>15,45</sup>. In addition, the kinetic measurements were carried out by varying the partial pressure of one reactant while the other reactant was fixed. The rate of formation of  $H_2$  was calculated using Polymath 6.1 software and the results are provided in Figure S7, SI. The rate of formation of  $H_2$ increases with increase in the partial pressure of CH<sub>4</sub> and decreases with increase in partial pressure of CO<sub>2</sub>, which is presented in the Figure S7(A) and S7(B). The higher rate of H<sub>2</sub> formation obtained with partial pressure of  $CO_2$  could be attributed to strong influence of methane cracking which yield carbon and H<sub>2</sub> which is consistent with the kinetic study of DRM reaction using SmCoO<sub>3</sub> perovskite catalyst<sup>46,47</sup>. Figure 3(D) represents the stability test of siloxene/Ni catalyst over a time of 240 minutes recorded at a temperature of 900 °C. It showed

that the stable conversion efficiency (almost close to the initial value) over a long time, indicating that the superior stability of siloxene/Ni catalyst <sup>48</sup>.

The major issue limiting the reusability of the catalyst is the deposition of carbon on the surface during DRM reaction <sup>49,50</sup>. Therefore, we have examined the morphological and spectroscopic analyses of the recovered spent catalyst for understanding the nature of carbon deposited on their surface. The FE-SEM micrographs of spent catalyst (Figure 4(A-D)) obtained under various levels of magnifications dictates the formation of carbon nanostructures on the surface of siloxene/Ni foam after the DRM reaction. The formation of carbon on the surface of siloxene/Ni catalyst might be due to the methane cracking reaction during the DRM reaction <sup>49,50</sup>. The EDS mapping and spectrum of spent catalyst (Figure 4 (E-J)) also confirms the deposition of carbon components in addition to the Ni, Si and O elements over the surfaces. The laser Raman spectrum of spent catalyst (Figure S8, SI) shows the presence of a sharp band at 515 cm<sup>-1</sup> and two broad bands at 1360 and 1570 cm<sup>-1</sup>, respectively. The sharp band at 515 cm<sup>-1</sup> corresponds to Si-Si bonding of the siloxene sheets and the observed peak merging in comparison with untreated siloxene) can be explained using the thermal treatment effects of siloxene at hightemperatures<sup>51</sup>. The two broad bands observed at 1360 and 1585 cm<sup>-1</sup> can be arised from the D and G band of deposited carbon on the siloxene/Ni catalyst <sup>52</sup>. The core-level XPS spectrum of Si 2p, O 1s, and C 1s of the spent catalysts are provided in Figure S9 (A-C), SI. In comparison with the core-level Si 2p spectrum of siloxene/Ni catalyst before and after the DRM reaction, significant changes were observed. The peak observed at 99.5 eV (Si-Si bonding) in the untreated siloxene/Ni sheets is diminished whereas peak due to Si-O bonding (102 -104 eV) is preserved even after the DRM process (Figure S9 (A), SI). This is due to thermal effects of siloxene sheets in which oxygen moieties in the siloxene react with Si-Si networks resulting in

the formation of Si-O bonding <sup>51,53</sup>. No noticeable changes in the O 1s spectrum (Figure S9 (C), SI) of spent catalyst have been observed after the DRM process. The core-level C 1s spectrum (Figure S9 (D), SI) indicated that the deposited carbon is sp<sup>2</sup> type <sup>54,55</sup>. These studies confirmed the deposition of sp<sup>2</sup>-type carbon on the surface of the siloxene/Ni catalyst; thus, reusability of the spent catalyst is questionable. Therefore, making use of spent catalysts in other sectors is highly desirable.

In general, carbon materials are widely used as an absorbent of industrial wastes, an additive for photocatalyst, electrocatalyst, and electrodes for electrochemical energy storage devices (such as supercapacitors and batteries) and so on<sup>56,57</sup>. Both Ni foam and siloxene sheets in the spent catalyst are widely used as the current collector and electrode materials in electrochemical energy storage devices, respectively <sup>58,59</sup>. Therefore, the development of a supercapacitor electrode using the carbon deposited spent catalyst will be an immense benefit in terms of WtE concept. The energy storage properties of carbon/siloxene/Ni based coin-cell type SSC were studied via sandwiching two ideal spent catalyst electrodes in between a Celgard separator filled with 1 M TEABF<sub>4</sub> electrolyte. Electrochemical studies such as cyclic voltammetry (CV), galvanostatic charge-discharge (CD) analysis, electrochemical impedance spectroscopic techniques (EIS), and long-term cyclic stability tests were performed in this work to study the usefulness of spent catalyst-based SSC. At first, CV tests were performed to understand the fundamental charge-storage kinetics and to determine the operating voltage window (OVW) of the carbon/siloxene/Ni SSC. Figure 5(A-C) represents the CV profiles of the carbon/siloxene/Ni SSC recorded at different levels of applied scan rates (from 5 to 1000 mV s<sup>-1</sup>). The CV profiles demonstrated that the fabricated carbon/siloxene/Ni SSC could operate over an OVW of 3.0 V, thanks to the ionic liquid electrolyte for such high voltage operation which can

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lead to enhanced energy density compared to aqueous electrolytes <sup>60</sup>. The nature of the CV profiles recorded at low scan rates (Figure 5(A)) indicated the presence of typical rectangular shaped curves as an indication of electric double layer capacitance (EDLC) in the carbon/siloxene/Ni SSC which is similar to that observed in reported carbon- based SSCs <sup>61</sup>. The small redox peak due to ion-intercalation/de-intercalation kinetics which usually appeared in the siloxene based SSCs is not observed in the CV profiles of carbon/siloxene/Ni SSC<sup>28</sup>. This is due to the high amounts of carbon deposited on the surface of siloxene/Ni foam which hinder the electrochemistry of siloxene sheets whereas the surface adsorption/desorption kinetics of carbon at the outer surface is highly evidenced in the CV profiles. The shape of CV profiles changed from rectangular to parallelogram-like shapes with an increase in scan rate from 100 to 1000 mV  $s^{-1}$  (Figure 5(B,C)), that is, due to the internal resistance of the electroactive material  $^{62}$ . The specific device capacitance of the fabricated carbon/siloxene/Ni SSC was determined from the CV profiles, and the results are summarized in Figure 5(D). The carbon/siloxene/Ni SSC possess a high device capacitance of 36 F g<sup>-1</sup> at a scan rate of 5 mV s<sup>-1</sup> which is quite comparable to carbon based SSC using ionic liquid electrolyte<sup>63</sup>. With an increase upto 5-, 10-, and 20- fold of scan rates, the carbon/siloxene/Ni SSC retains a specific device capacitance of about 68.42, 58,80, and 49.83 % of its initial capacitance highlighting the better rate capability of the carbon/siloxene/Ni SSC <sup>64</sup>. Figure 5(E) represents the Nyquist plot of the carbon/siloxene/Ni SSC with respect to the applied frequency. It revealed the presence of a semi-circle at the highfrequency region followed a straight line as the low- frequency region. The semi-circle observed at the high-frequency region can be related to the non-charging behavior of the carbon/siloxene/Ni SSC which is due to the charge-transfer resistance occurred at the electrode/electrolyte interface <sup>65</sup>. The equivalent series resistance (ESR) and charge-transfer

resistance ( $R_{ct}$ ) of the carbon/siloxene/Ni SSC are found to be about 2.24 and 42.42  $\Omega$  as determined from the Nyquist plot. The presence of a straight line or Warburg line running parallel to the imaginary axis of the impedance at the low- frequency region indicates the synchronous charging behavior of the carbon/siloxene/Ni SSC. This is due to the frequency dependent electrolyte ion-diffusion occurred at the carbon/siloxene/Ni surface <sup>66</sup>. Figure 5(F) represents the Bode phase angle plot of the carbon/siloxene/Ni SSC with respect to applied frequency. It showed that the phase angle at the low-frequency region is about 62°, which arises due to the combined effect of carbon deposited siloxene/Ni foam. The characteristic relaxation time (determined from the Bode phase plot) of the carbon/siloxene/Ni SSC is found be 12 sec using the relation ( $\tau$ =1/f<sub>o</sub>) which is comparable to those of the carbon based SSC <sup>67</sup>.

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The CD profiles of the carbon/siloxene/Ni SSC were recorded using different levels of applied current ranges (from 1 to 25 mA) as shown in Figure 6(A). The CD profiles show the presence of quasi-symmetric nature which revealed the occurrence of EDLC-type charge-storage mechanism in the carbon/siloxene/Ni SSC <sup>68</sup>. The high current ranges result in rapid charging and discharge rates, whereas the low current ranges result in slow charging and discharge rates which is due to the effect of time constraints faced by electrolyte at various applied current ranges <sup>69</sup>. The effect of applied current ranges on the specific device capacitance of the carbon/siloxene/Ni SSC is provided in Figure 6(B). A high specific device capacitance of 24.65 F g<sup>-1</sup> was obtained for the carbon/siloxene/Ni SSC from the CD profiles recorded using an applied current of 1 mA. The carbon/siloxene/Ni SSC retains a specific device capacitance of 57.87 % when the applied current range is increased upto to five- fold. Figure 6(C) depicts the energy and power density of the carbon/siloxene/Ni SSC in the form of a Ragone plot. From Figure 6(C), it is evident that the carbon/siloxene/Ni SSC possess a high energy density (30.81

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Wh Kg<sup>-1</sup>) and power density (625 W kg<sup>-1</sup>) using a constant current of 1 mA. With a 25- fold increase in current density, the energy density decreases upto 5.99 Wh Kg<sup>-1</sup> whereas the power density reaches upto 15,625 W Kg<sup>-1</sup>, respectively. Remarkably, the high power density of 15,625 W Kg<sup>-1</sup> for the carbon/siloxene/Ni SSC attains the power target of PNGV (Partnership for a New Generation of Vehicle) systems, thus, making their candidature in electric vehicle applications<sup>70</sup>. The energy/power performance metrics of carbon/siloxene/Ni SSC is also compared with recently reported carbon- and 2D materials based SSCs using organic electrolyte in Table S2, SI. Encouragingly, the performance metrics of carbon/siloxene/Ni SSC is comparably higher than many of the reported SSCs such as activated carbon based SSC (25 Wh Kg<sup>-1</sup> and 100 W Kg<sup>-1</sup>)<sup>71</sup>. rGO-CMK-5 SSC (23 Wh Kg<sup>-1</sup> and 200 W Kg<sup>-1</sup>)<sup>72</sup>, siloxene SSC (5.08 Wh Kg<sup>-1</sup>, 375 W Kg<sup>-1</sup>)<sup>28</sup>, HT-siloxene SSC (6.64 Wh Kg<sup>-1</sup>, 675 W Kg<sup>-1</sup>)<sup>51</sup>, and so on. Figure 6(D) picturizes the long term cyclic stability of the carbon/siloxene/Ni SSC recorded using an applied current of 7.5 mA over 10,000 cycles which highlight their superior cyclic stability. After long term cyclic tests, the carbon/siloxene/Ni SSC retains a specific device capacitance of 90 % to its initial capacitance <sup>73</sup>. These values are considerably better compared to the state of art of ionic liquid-based SSCs <sup>72,74,75</sup>. The inset of Figure 6(D) shows the practical applications of fully charged carbon/siloxene/Ni SSC to lit up different colored LED lamps. These electrochemical studies dictate the better charge-storage properties of the fabricated carbon/siloxene/Ni SSC derived from the residual catalytic byproducts of DRM reactions.

### 3. Conclusions:

The key findings of this work demonstrated the significant use of siloxene/Ni foam as a suitable catalyst for DRM reaction for enhancement in syngas production. The better catalytic properties of siloxene/Ni catalyst to convert of methane and CO<sub>2</sub> into syngas will be highly

useful for producing value-added products via Fischer–Tropsch route, thereby highly appropriate for reducing the global CO<sub>2</sub> emissions. The morphological and spectroscopic investigation on the spent catalyst after the DRM process indicated the deposition of carbon on the surface of the siloxene/Ni catalyst. A smart strategy has been adopted to recycle the spent catalyst (carbon deposited siloxene/Ni) by utilizing them as supercapacitor electrodes. The fabrication SSC using spent catalyst as electrodes displayed remarkable energy density (30.81 Wh Kg<sup>-1</sup>) and highpower density (15,625 W Kg<sup>-1</sup>) which are superior to that of reported carbon based SSCs. Considering the required cost of carbon production for supercapacitor electrode, and the achieved remarkable performance metrics of SSCs using spent catalyst, this strategy of utilizing the carbon deposited spent catalyst as supercapacitor electrodes will provide new insights on the waste to energy applications.

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### **Figure captions:**

**Figure 1.** (A) Schematic representation illustrating the preparation of siloxene sheets via topochemical de-intercalation of calcium atoms from layered calcium silicide immersed in ice cold HCl, (B) High resolution transmission electron micrograph (HR-TEM) of siloxene sheet. The elemental mapping showing the distribution (C) Si atoms and (D) O atoms present in the siloxene sheets given in (B), and (E) represents the elemental mapping spectrum of siloxene sheets.

**Figure 2.** Schematic explanation of this work. The siloxene coated Ni foam was examined as a catalyst for the dry reforming of methane (DRM) via the reaction between methane and carbon dioxide gases to produce syngas ( $H_2 + CO$ ). The recovered catalyst after DRM process shows the formation or deposition of carbon on the surface due to methane decomposition and the recovered catalyst (carbon coated siloxene/Ni foam) is used as electrode for symmetric supercapacitor utilizing ionic liquid electrolyte.

**Figure 3.** Catalytic performance of siloxene/Ni catalyst for DRM reaction. (A) Conversion efficiencies of methane and carbon dioxide (CO<sub>2</sub>) as a function of temperature, (B) Concentration of produced synthetic gas as a function of temperature, (C)  $H_2$ /CO ratio of siloxene/Ni catalyst obtained at different temperatures, (D) and conversion efficiencies of methane at 900 C over a period of 240 min for the siloxene/Ni foam catalyst.

**Figure 4.** Surface morphology and composition analysis of siloxene/Ni catalyst after DRM reaction. (A-D) represents the field emission scanning electron micrograph of carbon deposited

21

siloxene/Ni catalyst recovered after DRM process, (E-I) elemental mapping analysis of carbon deposited siloxene/Ni catalyst with (E) being the overlay micrograph, and (F-I) represents the elemental maps of Ni, Si, O, and C elements on the surface of recovered catalyst. (G) EDX spectrum of recovered catalyst.

**Figure 5.** Electrochemical performances of carbon/siloxene/Ni electrode based symmetric supercapacitor using 1 M TEABF<sub>4</sub> electrolyte. (A-C) Cyclic voltammetric profiles of carbon/siloxene/Ni supercapacitor recorded using different levels of scan rates from 5 to 1000 mV s<sup>-1</sup>, (D) Effect of scan rates on the specific device capacitance of carbon/siloxene/Ni supercapacitor.

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**Figure 6.** Performance evaluation of carbon/siloxene/Ni supercapacitor using 1 M TEABF<sub>4</sub> electrolyte. (A) Charge-discharge profiles of carbon/siloxene/Ni supercapacitor recorded at different applied current ranges (from 1 to 25 mA), (B) Effect of applied current ranges on the specific device capacitance of carbon/siloxene/Ni supercapacitor, (C) Ragone plot of carbon/siloxene/Ni supercapacitor indicating their superior performance metrics over reported carbon based supercapacitors using ionic liquid electrolytes, (D) Long term cyclic stability tests of carbon/siloxene/Ni supercapacitor over 10,000 cycles of continuous charge-discharge analysis and the inset in (D) represents the practical applications of fully charged carbon/siloxene/Ni supercapacitor (upto 3.0 V) to glow up LED lamps. The references in inset of Figure 6(C) are indexed in the Table S1, supporting information of this article.



Figure 1.



Figure 2.



Figure 3.







Figure 5.



Figure 6.